CoFe ALLOY FILM AND PROCESS OF MAKING SAME

BACKGROUND OF THE DISCLOSURE

5   1. **Field of the Invention**

The present invention is directed to a CoFe soft magnetic thin film alloy having magnetic properties well suited for use in the fabrication of thin film

10   magnetic recording heads and a process for making same. More specifically, the present invention is directed to a CoFe alloy thin film in which the iron constituent is present in a concentration of between about 55 wt.% and 75 wt.% iron and a process for making same.

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The application of this high saturation magnetization CoFe thin film also includes magnetic shields for magnetoresistive read heads, magnetic actuators which may require high moment low Hc materials,

20   application in Micro-Electro Mechanical Systems (MEMS), soft magnetic underlay in magnetic perpendicular recording disk and other applications in electronics. All the above areas require thin electroplated magnetic films because cast materials cannot be used.

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2. **Background of the Prior Art**

The ever expanding demand for greater storage density in magnetic recording systems has correspondingly

30   led to increased demand for magnetic storage media with increased coercivity and higher a real storage density. In order to write to these higher coercivity media it is necessary to have write heads which will put out a higher

magnetic flux. Write heads which put out a higher magnetic flux must be made of magnetic pole materials with a higher saturation magnetization.

5   At present, the highest moment alloy films commercially available are nickel-iron alloys having a saturation magnetization of about 1.75 Tesla. Higher moment alloys are known in the art. These higher moment alloy films are electrodeposited films of an alloy of

10   cobalt-nickel-iron and cobalt-iron-copper having a saturation magnetic moment of 1.9 to 2.0 Tesla.

In spite of these advances in the development of write head materials, there is a continuing need for

15   the development of magnetic thin films having even higher magnetic moment values.

Although cobalt-iron (CoFe) alloys in the 55-75 wt.% Fe range are known to provide high saturation

20   magnetization, such alloys have been formulated by casting. Obviously, the formation of a very thin film, suitable for use in write head applications, from a cast alloy is not obtainable. The fabrication of such a film by sputtering, vapor deposition and electroplating have

25   been attempted. Sputtering does not produce a film having anisotropic characteristics, which is essential in write head applications. Vapor deposition results in course grained films which are also unsuitable in this application. Electrodeposition, however, represents a

30   most promising method to form improved thin film CoFe alloy thin films for application as write heads.

Past attempts to produce high-iron CoFe alloy electrodeposited films have failed to generate films having satisfactory magnetic and mechanical properties. Typical electrodeposited CoFe films have high magnetic

5   coercivity, poor or non-existent magnetic anisotropy, saturation magnetization (4πMs) substantially lower than the theoretical 2.40-2.45 Tesla, and are so stressed that they cannot be plated to a useful thickness (which in write heads is in the 1-3 micron range) without

10   delamination. This poor performance can be ascribed at least in part to the incorporation of oxygen into the electroplated CoFe film during deposition, a characteristic which does not occur when a CoFe alloy is cast. Thus, new thin film CoFe alloys and new processes

15   for making such films which are substantially free of oxygen represents a well established need in the art.

CoFe-containing alloys, including films of such alloys, as well as processes for their manufacture, are

20   known in the art. Examples of the most pertinent of such art are included hereinbelow.

U.S. Patent 4,756,816 describes a process for the electrodeposition of a cobalt-iron alloy on a

25   substrate. This process occurs in an aqueous electrolytic plating bath. The cobalt-iron alloy has an approximate cobalt to iron weight ratio of 90:10. The plating solution also has sodium saccharin, dodecyl sodium sulfate and wetting and buffering agents. The

30   CoFe thin film that results from using the disclosed process has near zero magnetostriction, acceptable permeability for use as a magnetic head, a highly

stabilized magnetic domain and approximately 2.0 Tesla
saturation magnetization. Magnetic heads fabricated from
such films are well suited for use with high coercivity
media for high density magnetic recording.

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U.S. Patent 5,372,698 is directed to a process
of forming a thin film magnetic read/write head having a
thin film magnetic core and a substrate upon which a
crystalline magnetic alloy of cobalt, iron and boron is
10   electrodeposited. The cobalt-iron-boron core is 90%
cobalt and has a saturation magnetization of 1.9 Tesla.

Japanese Patent Publication 6036929 sets forth
a wet plating method for making a magnetic thin film.
15   The method involves plating a cobalt-iron-tin alloy in
which the tin constituent is present in a concentration
of 8 to 25 wt.%.

Japanese Patent Publication 4-229607 discloses
20   a magnetic thin film formed in an electroplating method
in which the coating alloy is mainly cobalt but also
includes iron in a concentration of 2 to 15 wt.% and
sulfur in a concentration of 500 to 2,000 ppm. The
sulfur constituent is provided by a sulfinic acid group
25   or its salt, a sulfonic acid group or its salt, a
sulfonimide group, a sulfonamide or a thiourea-based
compound and mercaptodicarboxylic acid. However, the
alloy composition disclosed in this Japanese patent
refers to a high cobalt content alloy (85 wt.% to 98 wt%)
30   and does not cover alloys containing lower Co
concentration. In addition, although we have no
indication of the value of the saturation magnetization,

we can estimate its value being below 2.5 Telsa based on the general trend among high cobalt-content CoFe alloys.

Japanese Patent Publication 2-107,737 teaches an amorphous soft magnetic film which includes cobalt, iron, tin and phosphorus.

U.S. Patent 2,654,703 describes the electrodeposition of bright nickel, cobalt, and alloys thereof from acid baths, using aryl (aromatic) sulfinic acids or salts thereof. The plating of cobalt-iron alloys is not claimed; in fact, sulfinates are said to retard the rate of codeposition of iron if ferrous salts are added to such baths, which, if true, would obviously be undesirable in the plating of high-iron cobalt alloys. No mention is made of any magnetic properties or uses of these alloys.

U.S. Patent 5,587,026 concerns a ferromagnetic film which has high saturation magnetic flux density. The film is an alloy of cobalt, iron and a metal selected from the group consisting of tantalum, titanium, zirconium, hafnium, molybdenum and tungsten. The addition of a ternary element to the CoFe alloy system can achieve relatively high saturation magnetic flux density (4nMs) between ~1.5 to 1.9 Tesla and after high temperature annealing a coercivity lower than 1.88 Oersteds. The cobalt content of the ferromagnetic film is 73 at% to 94 at%.

U.S. Patent 4,306,908 is directed to a ferromagnetic amorphous alloy having the formula

$(Co_xNi_yFe_z)_aM_bG_c$, where M is Cr, Mo and/or W; G is Zr, Hf and/or Ti; $x=1-y-z$; $0 \leq y \leq 0.2$; $0 \leq z \leq 0.7$; $a=1-b-c$; $0 \leq b \leq 0.5$; and $0.05 \leq c \leq 0.2$.

U.S. Patent 4,933,026 involves a soft magnetic cobalt-iron alloy which includes 0.15% to 0.5% Ta, Nb or mixtures thereof. The cobalt constituent of the alloy is present in a concentration of between about 33% and 55%. This alloy is stated to be operable at temperatures as high as between 960° and 980°C, up to 100°C above the highest possible operable temperature of earlier approximately equal weight cobalt-iron alloys. The cast alloy of this disclosure is fabricated by vacuum melting and hot rolling a cast ingot to 2.5 mm thickness, reheating the strip to above the order-disorder temperature, i.e. about 800°C, and quenching in a brine solution below 0°C. However, the use of the very high temperatures (above 1500C) required in the production of CoFe cast alloy is not compatible with the fabrication of magnetic recording thin film heads which makes this CoFe alloy unusable for such an application. More generally, the casting process of this patent is not suitable for the preparation of thin film structures.

U.S. Patent 4,925,502 provides a soft cobalt-iron alloy which consists essentially of 35% to 60% by weight Co; 0.03% to 2% by weight Al and the remainder iron. This alloy is formed by compacting and sintering cobalt, iron and aluminum or iron-aluminum powders. The sintering process used in the '502 patent implies the application of very high temperatures (~1400C) and is consequently not compatible with the fabrication of magnetic recording thin film heads and the like.

An article by L.H. Chen et al. entitled "Soft-Magnetic Properties of Fe-Co-B Thin Films for Ultra-High-Frequency Applications" in J. Appl. Physics, Vol. 87, Number 9, pp 5858-5860 (May 2000) describes an amorphous

5   CoFeB thin film sputter deposited at a composition of 67 at% iron, 18 at% cobalt and 15 at% boron. Although this thin film exhibits a very low coercivity of about 0.3 Oersted, the saturation magnetization is very low ($4\pi Ms$ ~1.75 Tesla). Moreover, by conventional RF magnetron

10   sputtering technique, a perpendicular magnetic anisotropy tends to occur easily, which would be strongly detrimental to the performance of magnetic recording thin film heads.

15   An article by S.S. Abd El Rehim et al., "Electroplating of CoFe Alloys from Aqueous Acetate Bath" in Trans. IMF, 2000, 78 (1), pp 41-42 shows CoFe thin films with a composition ranging from about 43 % up to about 66 % iron (no indication if they are weight or

20   atomic percentages). The alloy composition disclosed in this article has microcracks and is consequently not suitable for the fabrication of magnetic recording thin film heads and the like. Moreover, the authors do not give any indication concerning the magnetic properties of

25   these CoFe alloys.

The full range of CoFe compositions has been investigated by E.M. Kakuno et al. in "Structure, Composition, and Morphology of Electrodeposited Co_xFe_{1-x}

30   Alloys" in J. Electrochem. Soc., Vol. 144, No. 9, September 1997, pp. 3222-3226 from an additive-free sulfate-based plating bath. The Co_xFe_{1-x} thin films with

an alloy composition varying from x=1 to 0 show heterogeneous morphology and composition and are then not suitable for the fabrication of magnetic recording thin film heads and the like. No indication of the magnetic

5   properties of these alloys is given in this article.

In U.S. Patent 4,208,254, the patentees disclose a method of electrodepositing a CoFe alloy having a composition of 7.5-55 wt.% iron, the remaining

10   being cobalt, from a fluoride-containing bath. No saturation magnetization value is given in this patent disclosure.

Soft magnetic amorphous CoFeP alloys have been

15   reported in the literature. For example, J. Herretos et al., "Preparation of Fe-Co-P Amorphous Alloys by Electrodeposition" in J. of Non-Crystalline Solids, 201 (1996) pp. 102-109 have electrodeposited a $Fe_{56}Co_{30}P_{14}$ alloy with a coercivity of about 2 to 5 Oersteds. There

20   is no indication of saturation magnetization. Although amorphous CoFeP alloys have been shown to exhibit excellent soft magnetic properties, they generally have a lower saturation magnetization due to the addition of glass forming agent in relatively high concentrations.

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Another type of amorphous CoFe alloy is obtained by the addition of boron as described in U.S. Patent 5,372,698 where the patentees disclose an electrodeposited CoFeB with an iron content between about

30   7 wt.% and about 12 wt.%, a boron content between about 0.1 wt.% and about 2.0 wt.%, the remaining being cobalt and having a saturation magnetization (4πMs) of about 1.9

Tesla and a coercivity of about 1.0 Oersted. Despite
good soft magnetic properties, the cobalt content (about
90 wt.%) of this alloy is between 25 wt.% and 45 wt.%.
Moreover, the alloy of this patent has a low
magnetization.

An electrodeposited CoFe alloy containing
vanadium is presented by Arcos et al., "Direct and Pulse
Current Electrodeposition of Ternary CoFeX, CoNiX and
NiFeX Thin Film Alloys" in Proc. of the 4th Int. Symp. on
Mag. Mat. Proc. and Dev., L.T. Romankiw and D.A. Herman,
Jr. Eds, 95-18, (1995), pp. 563-569. CoFeV
electrodeposites having a magnetic moment of about 2.0
Tesla are presented in this study. However, no clear
indication of the alloy composition and no indication of
the coercivity is provided. Furthermore, the saturation
magnetization of about 2 Tesla is too low for this
material to be used in the fabrication of advanced
magnetic recording thin film heads.

The addition of copper to the electrodeposited
CoFe alloy is disclosed by Andricacos et al. in U.S.
Patent 5,582,927 where a $Co_xFe_yCu_z$ alloy with a
composition in the range of about 65 wt.% to 92 wt.%
cobalt, about 6 wt.% to 15 wt% iron and about 2 wt% to 20
wt.% Cu has been electrodeposited. This alloy has a high
saturation magnetization (4nMs) in the range of 1.6 Tesla
to 2.4 Tesla and a coercivity of less than 1 Oersted.
However, these excellent soft magnetic properties require
a very low iron content CoFe alloy, i.e., less than 15
wt%.

In U.S. Patents 4,014,759 and 4,053,373 an α-hydroxy sulfone compound, which is the reaction product of an aromatic sulfinate and an aldehyde or dialdehyde, is used in iron-containing baths to improve plating of 15 wt.% to 70 wt.% Fe-containing alloys of nickel or cobalt or nickel and cobalt.

Finally, Liu, et al., Journal of Applied Physics, Vol. 87, no. 9, 5410-5412 (2000) describes the electrodeposition of cobalt-iron-nickel alloy thin films for magnetic recording heads. This deposition occurs in the absence of sulfur-containing additives. Although the coercivity of these films was about 1 Oe, the saturation magnetization was only 2.0 Tesla.

SUMMARY OF THE INVENTION

A new alloy film and process for making that soft magnetic thin film alloy has now been developed which provides a saturation magnetization ($4\pi Ms$) above the maximum saturation magnetization ($4\pi Ms$) obtained by commercially available soft magnetic thin film alloys. The newly developed soft magnetic thin film is particularly suitable for use as a write head in magnetic recording.

The soft magnetic thin film alloy of the present invention is a CoFe alloy fabricated in an electroplating process from an aqueous plating bath to produce a smooth, bright surfaced film indicative of the substantial absence of oxygen and iron oxide. A paddle cell with continuous filtration is used for the

electroplating process. A magnetic field of 700-800 Gauss can be used during plating to magnetically orient the electroplated CoFe alloy film. The resulting soft magnetic thin film alloy has relatively low stress and can be plated to thickness up to 2 microns.

In accordance with the present invention a cobalt-iron film comprising between about 55% and about 75% iron and the remainder cobalt, said percentages being by weight based on the total weight of the alloy, is provided. The film is further characterized by a maximum saturation magnetization (4πMs) of at least about 2.30 Tesla.

In further accordance with the present invention a process of making the cobalt-iron alloy film is disclosed. In that process the cobalt-iron alloy film is electrodeposited from an aqueous medium which includes one or more ferrous salts; one or more cobaltous salts; a buffer having a pKa of about 6 to about 8 which does not co-deposit into the plated CoFe thin film alloy; one or more mono- or polycarboxylic acids having pKa(s) in the range of between about 3.5 and about 5.5; an aromatic sulfinic acid or a salt thereof; optionally, a chloride salt; and optionally, a surfactant.

BRIEF DESCRIPTION OF THE DRAWINGS

The present invention may be better understood by reference to the drawings of which:

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Figure 1 is a graph of easy axis coercivity (H_c) as a function of weight percent iron of a CoFe soft magnetic thin film alloy;

5   Figure 2 is a graph of saturation magnetization ($4\pi M_s$) as a function of weight percent iron of a CoFe soft magnetic thin film alloy;

Figure 3 is a graph of film resistivity (in $\mu\Omega$-cm) as a function of weight percent iron of a CoFe soft
10   magnetic film alloy;

Figure 4 is a graph of film stress as a function of weight percent iron of a CoFe soft magnetic
15   thin film alloy;

Figure 5 is a graph of hard axis coercivity (H_c) as a function of weight percent iron of a CoFe soft magnetic thin film alloy; and
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Figure 6 is a graph of magnetic anisotropy (H_k) as a function of weight percent iron of a CoFe soft magnetic thin film alloy.

25   **DETAILED DESCRIPTION**

The cobalt-iron (CoFe) alloy film of the present invention, characterized by a bright, smooth finish, is substantially free of oxygen and iron oxide.
30   The CoFe film is preferably a thin film having a thickness up to 2 microns.

The CoFe soft magnetic thin film alloy comprises about 55% and about 75% iron and the remainder, between about 25% and about 45%, cobalt, the percentages being by weight, based on the total weight of the alloy film. Preferably, the constituency of the CoFe alloy film is about 60% to about 66% iron and the remainder, between about 34% and about 40%, cobalt. More preferably, the CoFe alloy film is present in a concentration of between about 62% and about 65% iron and the remainder, between about 35% and about 38%, cobalt.

The CoFe alloy film is further defined by a maximum saturation magnetization, also denoted by the scientific notation, $4\pi M_s$, of between about 2.3 and about 2.5 Telsa. Preferably, the $4\pi M_s$ of the CoFe alloy film is in the range of between about 2.32 and about 2.50 Tesla. More preferably, the maximum saturation magnetization of the CoFe alloy is in the range of between about 2.38 and about 2.53 Telsa.

The CoFe alloy film is anisotropic, as defined by an easy axis coercivity (H_{ce}) of no more than 22 Oersted (Oe), which drops to no more than about 12 Oe upon annealing; a hard axis coercivity (H_e) of no more than about 17 Oe, which drops to no more than about 9 Oe upon annealing; and a magnetic anistrophy (H_k) of no more than about 30 Oe, which is substantially unchanged upon annealing.

Preferably, the anisotropic properties of the CoFe alloy film are manifested by an easy axis coercivity of no more than about 17 Oe, which drops to no more than

about 8 Oe upon annealing; a hard axis coercivity of no more than about 7 Oe, which drops to about 3.5 Oe upon annealing; and a magnetic anisotropy of no more than about 24 Oe which is substantially unchanged upon

5   annealing.

More preferably, the CoFe alloy film has the following anisotropic properties: an easy axis coercivity of no more than about 15 Oe, which drops to no more than

10   about 6 Oe upon annealing; a hard axis coercivity of no more than about 5 Oe, which drops to no more than about 2.5 Oe upon annealing; and a magnetic anisotropy of no more than about 20.5 Oe, which is substantially unchanged upon annealing.

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The CoFe alloy film is further characterized by a specific resistivity in the range of between about 17 and about 65 $\mu\Omega$-cm. Preferably, the CoFe alloy film has a specific resistivity of between about 24 and about 42

20     $\mu\Omega$-cm. Most preferably, the specific resistivity is in the range of between about 30 and about 40 $\mu\Omega$-cm.

The CoFe alloy film is characterized by an internal mechanical tensile stress of between about 250

25   and about 800 MegaPascals (MPa). Preferably, the film is characterized by a stress of between about 470 and about 700 MPa. More preferably, the CoFe alloy film is characterized by a stress of between 600 and about 630 MPa.

30

The CoFe alloy film of the present invention is prepared by a process in which the film is electroplated

from an aqueous chemical plating bath. The plating bath is characterized by a pH of about 2.5 to about 3.5. The minimum pH is limited by hydrogen evolution and reduced current efficiency, and the maximum pH by the propensity

5   of ferrous ions to oxidize and precipitate as ferric compounds. Preferably, the pH is in the range of between about 2.8 and about 3.2.

The plating bath is an aqueous solution of one

10   or more ferrous salts, of which the anion is preferably sulfate; one or more cobaltous salts of which the anion is preferably sulfate; a buffer having a pKa of about 6 to about 8 which does not co-deposit into the plated CoFe thin film alloy, e.g. boric acid; one or more mono- or

15   polycarboxylic acids having pKa(s) in the range of between about 3.5 and about 5.5, e.g. acetic acid; an aromatic sulfinic acid or a salt thereof; optionally, a halide salt; and, optionally, a surfactant. Preferably, the pH of the plating bath is between about 2.8 and about

20   3.2. The plating solution is preferably recirculated continuously through a fine filter (0.2-0.5 micron) in order to avoid precipitation of ferric compounds.

The electroplating operation is conducted at an

25   average cathodic current density of between about 3 milliamperes/square centimeters (mA/cm^2) and about 40 mA/cm^2. Preferably, the average cathodic current density is in the range of between about 5 mA/cm^2 and about 30 mA/cm^2. More preferably, the plating operation is

30   conducted at an average cathodic current density of between about 10 mA/cm^2 and about 20 mA/cm^2. Various current versus time programs may be used in the plating,

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including, but not limited to, direct current, pulsed current, cathodic based sinusoidal current and pulsed reversed current. The electroplating may also be accomplished on various thin film electrically conductive substrates which have been properly prepared for plating (in a manner known by those skilled in the art). These substrates may include, but not are not limited to, nickel-iron alloys, nickel-cobalt alloys, iron-cobalt alloys, cobalt-nickel-iron alloys, iron-nitrogen alloys, iron-aluminum-nitrogen alloys, rhodium, ruthenium, platinum, gold, copper and palladium. An iron or a cobalt anode can be used in the plating equipment. Dimensionally stable anodes of platinized titanium, platinum, graphite or carbon can also be used. A cobalt anode is preferred as it undergoes anodic dissolution easily and does not cause substantial oxidation of the ferrous ion in solution.

Turning to the specific constituents of the plating bath, the mono or polycarboxylic acid is preferably acetic acid. Other monocarboxylic or polycarboxylic acids which may also be used include succinic acid, glutaric acid and methylsuccinic acid. Sugar alcohols, such as mannitol or sorbitol, may also be used as part of the buffer mixture.

The mono or polycarboxylic acid is provided in a concentration in the range of between about 0.01 Molarity (M) and 0.4M. Preferably, the carboxylic acid is present in a concentration of between about 0.02 M and about 0.33 M. More preferably, the carboxylic acid concentration ranges between about 0.02 M and 0.25 M.

The buffer, as suggested above, is preferably boric acid, which has been shown to have a pKa of 6 to 8 in the electroplating bath described here. Other buffers, which may also be used instead of boric acid,

5   include alkyl-substituted pyridines such as picolines and lutidines. In particular, such picolines and lutidines as 2-picoline and 2,6-lutidine are preferred. As stated above, buffers other than those recited above, which have a pKa of 6 to 8 and do not co-deposit into the plated

10   CoFe thin film alloy, can be employed.

This buffer is present in an amount in the range of between about 0.08 Molarity (M) and about 0.65 M; preferably, between about 0.16 M and about 0.49 M; and

15   more preferably, between about 0.32 M and about 0.44 M.

The halide salt employed in the plating bath is preferably a chloride or a bromide salt in which the cation is an alkali metal, an alkaline earth metal,

20   cobalt or iron. Other inorganic halides may be used provided that the cation produced during solvation does not plate into the thin film CoFe alloy. In addition, organic halides may be used provided they do not adversely affect the plating rate or plated film quality.

25   Of these, alkali metal halides are preferred. Of the alkali metal halides, sodium chloride is most preferred.

The halide salt constituent of the plating bath is present in a concentration of about 0.0017 Molarity

30   (M) to about 0.0342 M; preferably, between about 0.0051 M and about 0.0171 M; and more preferably, between about 0.0068 M and about 0.0120 M.

The inorganic cobalt salt of the plating bath is any soluble salt of cobalt. Among preferred soluble cobalt salts are hydrates. As indicated above, it is preferred that the cobalt salt be a sulfate although a

5   chloride or a bromide salt is acceptable.

The ferrous salt of the plating bath, like the cobalt salt, is any soluble ferrous salt. Also, like the cobalt salt, a preferred class of soluble ferrous salts

10   are hydrates. Indeed, in accord with the cobalt salts, sulfates are particularly preferred although a chloride or a bromide may be employed.

As those skilled in the art are aware, the

15   concentration of the cobalt salt in the electroplating bath, relative to the concentration of the iron salt, dictates the concentration of the electroplated CoFe alloy film. Thus, this concentration varies depending upon the desired constituency of the CoFe film.

20   Preferably, though, the range of iron metal ion (2+ valence) in the bath is in the range of about 0.10 Molarity (M) to about 1.50 M.

The aromatic sulfinic compound of the

25   electroplating bath is preferably an aromatic sulfinic acid or a salt thereof. The aromatic sulfinic salt form is preferable because aromatic sulfinic salts tend to be more soluble than aromatic sulfinic acids. The cation of the salt can be any metal ion that is inert under plating

30   conditions, e.g. sodium or potassium. The acid can be any sulfinic derivative of benzene or naphthalene, with optional additional substituents (on the aromatic ring)

that are inert under the plating conditions. Thus, such substituents as alkyl, chloro, and alkoxy may be present.

A preferred aromatic sulfinic compound is benzenesulfinic acid. More preferably, a sodium salt of a benzenesulfinic hydrate salt, the sodium dihydrate salt of benzenesulfinic acid, sodium benzenesulfinate dihydrate, is employed. Other aromatic sulfinic acids or salts that can be employed include sodium toluenesulfinate, sodium p-chlorobenzenesulfinate and the like.

The benzenesulfinate salt is present in the plating bath in a concentration of about 0.000061 Molarity (M) to about 0.001218 M; preferably, between about 0.000091 M to about 0.000914 M; and more preferably, between about 0.000122 M to about 0.000610 M. The sulfinate additive is slowly consumed both by plating and by air oxidation; therefore, periodic replenishment is needed.

It will be obvious to one skilled in the art that surfactants are useful for proper wetting of the substrate to be plated. They are also helpful in preventing gas bubbles from adhering to the surface of the substrate. However, the presence of a surfactant in the plating bath is not an essential part of this invention. If the use of a surfactant is desired, the surfactant provided in the plating bath may be Fluorad FC-95 or Fluorad FC-98, both being anionic surfactant products of the 3M Company. Other surfactants such as, but not limited to, sodium lauryl sulfate can also be

used. The surfactant constituent, if present, is used in a concentration of about 0.01-0.03 g/l for the Fluorad type surfactants and about 0.2-0.5 g/l for sodium lauryl sulfate.

The electroplating in this invention is performed at a temperature range between 10°C and 46°C. The best film properties of CoFe are achieved between 10° and 25°C.

The following examples are given to illustrate the scope and spirit of the present invention. Because these examples are given for illustrative purposes only, the present invention should not be interpreted as being limited thereto.

EXAMPLES

A series of examples were prepared wherein the CoFe alloy films were electroplated from a plating bath. The plating bath was an aqueous solution, having a pH of 3, of the following constituents whose concentrations are provided below, except for the cobalt and sulfate salt constituents whose concentrations varied to provide a range of concentration of the resultant CoFe alloy films. The examples included CoFe alloy films within and outside the present invention insofar as the iron concentration of the CoFe alloy film ranged between 35 wt% and 70 wt%. In all cases, the plating occurred at a current density of 10 to 20 mA/cm^2. During plating the temperature was maintained at 21.3°C accompanied by a paddle speed of 1 Hz.

These examples, within and outside the scope of the present invention, produced cobalt-iron alloy films. The films including their physical properties are summarized in the Table and are pictorially depicted in

5   Figures 1-6.

For illustrative purposes four examples of plating solutions, including the resultant alloy films, are set forth below. Since these examples are provided

10   for illustrative purposes only, the invention should not be deemed limited thereto.

EXAMPLE 1

Constituent	Concentration, g/l
Acetic acid	3
Boric acid	25
$CoSO_4 \cdot 7H_2O$	17.54
$FeSO_4 \cdot 7H_2O$	62.95
Sodium benzene sulfinate	0.09
FC-95 surfactant	0.01

This particular bath composition, having a molar ratio of Fe/(Fe+Co) of 0.784 yields of a film containing 72.37 wt% Fe and 27.63 wt% Co. This film, denoted in the Table as Alloy Film No. 26, is within the scope of the present invention.

EXAMPLE 2

Constituent	Concentration, g/l
Acetic acid	12
Boric acid	25
$CoSO_4 \cdot 7H_2O$	53
$FeSO_4 \cdot 7H_2O$	122
Sodium benzene sulfinate	0.09
FC-95 surfactant	0.01
NaCl	0.5

This particular bath composition, having a molar ratio of Fe/(Fe+Co) of 0.699, yields a film denoted in the Table as Alloy Film No. 16, within the scope of the present invention.

EXAMPLE 3

Constituent	Concentration, g/l
Acetic acid	12
Boric acid	25
$CoSO_4.7H_2O$	53
$FeSO_4.7H_2O$	102
Sodium benzene sulfinate	0.04
FC-95 surfactant	0.01
NaCl	0.5

The film produced by the above plating bath composition is set forth in the Table as Alloy Film No. 10. The film of this example was within the scope of the present invention.

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EXAMPLE 4

Constituent	Concentration, g/l
Acetic acid	12
Boric acid	25
$CoSO_4 \cdot 7H_2O$	53
$FeSO_4 \cdot 7H_2O$	42
Sodium benzene sulfinate	0.02
FC-95 surfactant	0.01
NaCl	0.5

The product of this plating bath composition produced Alloy Film No. 1, outside the scope of the present invention.

Alloy Film No.	Fe wt.%	Co wt.%	Hc (easy) (Oe)	Stress (Mpa)	4πMs (Tesla)	Specific Resistance μΩ-cm	Hk (hard) (Oe)	Hc (hard) (Oe)
1	35.22	64.78	50.32	139.3	2.14	8.76	124.5	48.78
2	40	60	46.02	223.3	2.26	8.89	118.9	47.69
3	41.7	58.3	46.05	136.1	2.3	9.71	111.2	45.53
4	44.37	55.63	40.38	198.9	2.32	10.31	103	42.11
5	45.88	54.12	31.8	289.7	2.36	11.27	91.9	37.39
6	49.39	50.61	26.96	383	2.46	12.55	73.97	28.02
7	50.47	49.53	25.17	211.1	2.4	14.37	45.88	24.2
8	52.74	47.26	21.29	299	2.39	15.87	33.41	16.92
9	54.98	45.02	21.29	380	2.39	17.35		
10	57.22	42.78	19.2	484.8	2.33	19.29	26.49	10.78
11	58.34	41.66	17.38	247.7	2.45	19.3	26.98	8.049
12	59.34	40.66	16.29	470.9	2.46	24.17		5
13	60.87	39.13	17.37		2.49	21.37	20.21	6.863
14	61.58	38.42	14.94	.	2.47	23.28	21.13	5.609
15	61.69	38.31	14.66		2.43			5
16	62.13	37.87	13.28	599	2.41	31.48	18.17	5.009
17	62.68	37.32	12.66	569.9	2.5	35.82	19.22	4.857
18	62.96	37.04	13.87		2.53			5
19	63.11	36.89	13.84		2.32			5
20	65.52	34.48	8.855	527.4	2.38	40.33	15.19	3.314
21	65.52	34.48	9.463	460.9	2.42	37.34	14.87	3.488
22	67.29	32.71	8.231	697.9	2.47	43.14	13.19	3.169
23	69.09	30.91	6.536		2.47	48.45	13.51	3.618
24	69.96	30.04	7.247		2.37		18.59	2.208
25	72.2	27.8	6.878		2.331		14.34	1.809
26	72.37	27.63	6.491		2.34		15.7	1.98
27	74.3	25.7	6.863		2.333		13.32	1.66

The above embodiments and examples are given to illustrate the scope and spirit of the present invention. These embodiments and examples will make apparent, to those skilled in the art, other embodiments and examples. These other embodiments and examples are within the contemplation of the present invention. Therefore, the present invention should be limited only by the appended claims.